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Ozone Modulation of Volatile Hydrocarbons Using Membrane Introduction Mass Spectrometry

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A new method that we describe as chemical modulation of volatile hydrocarbons is investigated using ozonolysis pretreatment and membrane introduction mass spectrometry (MIMS). This extension to the MIMS technique is intended to enhance the selectivity of MIMS for measuring hydrocarbons in the complex mixtures often encountered in polluted air samples. The test samples for this study were dilute (parts per billion by volume, ppbv) two-component hydrocarbon mixtures in synthetic air. Ozone reacted to completely suppress the MIMS signal from β-pinene in a mixture of toluene and β-pinene and the MIMS signal from cyclohexene in a mixture of cyclohexene and cyclohexane. As expected, the ozone reaction produced little attenuation of the MIMS signal from toluene and cyclohexane in the test mixtures. The basis of the method is that the products of the ozonolysis, which is rapid for alkenes, are polar compounds that are excluded by the membrane used here, as confirmed in this study. Since the modulation only affects unsaturated hydrocarbons (and other similar organic compounds), the method can be used to aid in quantitative analysis of volatile hydrocarbon compounds in air samples for air pollution monitoring.

Introduction

A new approach is reported to aid in the measurement of volatile hydrocarbons in complex gaseous matrixes (e.g., chemical plumes or other atmospheric air samples). The method seeks to improve the selectivity of the membrane introduction mass spectrometric method by selective pretreatment of the analyte mixture. Membrane introduction mass spectrometry (MIMS) is used to allow selective introduction of volatile and semi-volatile analytes into the ion source of a mass spectrometer via processes known collectively as pervaporation (*1*−*3*). Permeated analyte is usually ionized via electron ionization (EI) or chemical ionization (CI), and the parent and fragment ions are mass analyzed using traditional mass spectrometric methods. The membrane acts as an interface between the sample (vapor or solution) and the vacuum of the mass spectrometer (*1*−*3*). MIMS has proven valuable in the direct analysis of volatile organic compounds (VOCs) in aqueous (*4*−*7*) and air samples (*8*−*11*) and has been used in biological applications (*12*−*14*) and online environmental monitoring of industrial processes (*15*).

Analysis of VOCs in air has been conducted regularly in the last few decades because of the role of VOCs in ozone formation in urban areas and their relationship with aerosol production (*16*). Although there are proven techniques for the analysis of VOCs, the time per analysis is too long to allow for online monitoring. MIMS has emerged as an efficient technique for the direct online analysis of VOCs in water and air samples by demonstrating promising speed and trace-level detection capabilities in a robust measurement method (*7, 10, 11, 17*). However, the MIMS approach has the chief disadvantage of a lack of physical separation of sample mixtures (*18*). For mixtures of VOCs and especially hydrocarbons, extensive ion fragmentation tends to produce very complicated mass spectra and, hence, quantitation problems due to the fact that different parent compounds have common fragment ions. The lack of unique fragments for each analyte in the mixture makes it difficult to identify individual parent neutral species and to conduct a quantitative analysis based on their mass spectra.

To solve this problem, several techniques have been investigated including selective chemical ionization (*10*), tandem mass spectrometry (*19*), and multivariate calibration methods (*18*−*20*). In this work, an ozone chemical modulation step is included in hydrocarbon mixture analysis to reduce the complexity of the compound mass spectra. The membrane used in this work separates the volatile hydrocarbons from the sample matrix based largely on polarity. Reaction with ozone was used to convert the nonpolar alkenes in test mixtures of hydrocarbons to undetermined oxygenated compounds (aldehydes, ketones, etc.) (*21*) that are excluded by this membrane. Ozone reacts slowly with aromatic and saturated hydrocarbons, so little attenuation of these species is expected (*21*). The effect of the modulation is observed by comparing the mass spectra of a mixture before and after the ozone reaction, where the difference between the spectra is predominantly due to the modulated alkenes in that mixture.

Experimental Section

The MIMS system used in these experiments is similar in design to commercially available systems. It consists of an ion trap mass spectrometer (Magnum, Finnigan MAT, San Jose, CA) that is configured to accept a 0.5 in. diameter direct insertion capillary membrane probe through a vacuum adapter installed in the GC transfer line inlet port. Inside the 0.5 in. tubing are three 15 in. long, 0.08 in. o.d. stainless steel tubes. Two of the tubes are used to transport the gaseous sample to and from the capillary membrane, which is securely attached to the tubing ends. The other tube is used to deliver helium (UHP, Matheson Gas Inc.) to the ion trap at the required operating pressure. The helium flow also assists in the rapid and complete transport of the permeated sample through the 5.2 cm^3 internal volume of glass tube and Teflon adapter that mates with the GC inlet of the ion trap. The capillary membrane used in this work was Silastic laboratory tubing, 2.16 mm. o.d., 1.02 mm. i.d. (Dow Corning, Midland, MI). This tubing was used because it is readily available; in future work, we hope to be able to acquire thinner tubing, which should decrease the response time significantly. The exposed length of the capillary membrane within the glass tube and Teflon adapter was 15 cm. The entire MIMS system can be maintained at elevated temperatures and is typically held at 130 °C.

Flow injection analysis (FIA) was used for sample introduction via a 4-port gas injection valve (Valco Instruments Co. Inc.) In one valve position N_2 (UHP, Matheson Gas, Inc.) flows through the MIMS probe, while in the other position the sample flows through the membrane. The flows are

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regulated so that the N_2 and sample flows are at the same pressure and flow rate when flowing through the membrane. Between analyses, nitrogen gas passes through the membrane interface, which is heated to 130 °C, eliminating carry-over from previous samples and thus increasing reproducibility.

Pressurized standard mixtures (1−10 ppmv in 500 psig UHP nitrogen) of the hydrocarbons were prepared in a gas manifold. Variable hydrocarbon mixing ratios were delivered to the MIMS probe via a flowing dilution system consisting of three mass flow controllers (FC-260, Tylan Inc.) for N_2, the sample mixture, and O_2. The concentration of the hydrocarbons were adjusted by controlling the sample and N_2 flow rates, while the O_2 flow was kept constant at 20% of the total flow rate. The test compounds toluene (EM Science, 97%), β-pinene (Aldrich, 99%), cyclohexene (Acros Organics, 99%), cyclohexane (Fisher Scientific, 95%), and cyclohexanone (Mallinckrodt, 90%) were all used as delivered.

The mass spectra were recorded using 70 eV electron ionization. The mass spectral data were collected using the Finnigan Magnum ion trap control software in the GC mode (mass spectra as a function of time, typically three or more mass spectra per second.) Data were collected using both full mass scans (40−200 m/z) and the selected ion monitoring method, depending on the application.

The volatile hydrocarbon samples were analyzed with the FIA/MIMS system before and after the ozone reaction. Each experiment was performed in the following sequence: (i) A selected mixing ratio of the hydrocarbon samples was produced by the dilution flow system and analyzed via FIA/MIMS as explained above. Typically three cycles of the FIA were recorded per sample to check for reproducibility. (ii) An appreciable percentage (~2% as determined by ultraviolet absorbance measurements) of the oxygen flow was converted to ozone using a commercial ozonizer. (This is the maximum conversion efficiency attainable with our ozonizer, an older electrical discharge source of unknown make and model.) The ozonolysis takes place between the mass flow controller and the point where the ozone/oxygen merges with the nitrogen and hydrocarbon flows. Specifically, the ozone/oxygen flow is delivered through approximately 12 in. of 0.25 in. o.d. Teflon PFA tubing before joining the nitrogen/sample flow in a PFA "tee". The sample and nitrogen flows were previously joined in a PFA tee 4 in. upstream. The merged flow of sample, nitrogen, and ozone/oxygen flows through about 120 in. of 0.25 in. o.d. PFA tubing to allow for the ozone reaction to go to completion, before entering the delivery tube of our MIMS system described above. We surmise that most of the remaining ozone is rapidly destroyed by reaction on the inside of the stainless steel MIMS inlet tube. (iii) The ozone-treated samples were analyzed by FIA/MIMS, and the data were compared with those from before ozonolysis. (iv) The MIMS probe was flushed with clean N_2 for 5 min between experiments to eliminate any remaining ozone or hydrocarbon sample.

Results and Discussion

Two sets of two-component mixtures of volatile hydrocarbon compounds were examined in these proof of principle studies: toluene and β-pinene; cyclohexane and cyclohexene. A mixture of cyclohexene and cyclohexanone was also examined as a control. Ready calibration of the response of the FIA/MIMS system was then demonstrated using the toluene/β-pinene system. These mixtures were chosen because they are representative of those of interest in environmental VOC monitoring, particularly in areas that have petroleum industrial processes, and are rich in vegetation (*16*). For example, the Portland, OR, airshed typically receives extensive emissions from petroleum transfer stations and also contains the largest metropolitan forested area in the United States.

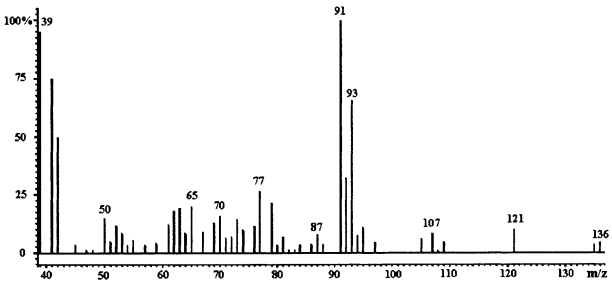

FIGURE 1. MIMS mass spectrum of the mixture containing 30 ppbv toluene and β-pinene.

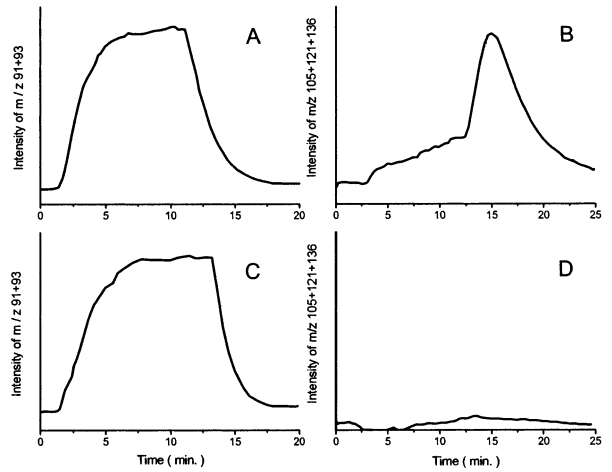

FIGURE 2. Selected ion profiles from a mixture with 30 ppbv each toluene and β-pinene: (A) *m/z* 91 + 93 (toluene and β-pinene) before the ozone treatment, (B) *m/z* 105 + 121 + 136 (β-pinene) before the ozone treatment, (C) *m/z* 91 + 93 (only toluene) after the ozone treatment, (D) *m/z* 105 + 121 + 136 (essentially absent) after the ozone treatment.

FIA/MIMS Mixture Analysis. Experiments with a mixture of toluene and β-pinene were conducted to determine whether the ozone modulation procedure was feasible with a mixture containing significant spectral overlap. Electron ionization of toluene produces m/z 91 as the main fragment ion, while β-pinene yields reasonably intense fragment ion signals at m/z 91, 93, 105, 121, and 136. Figure 1 shows the MIMS mass spectrum of a mixture containing 30 ppbv each of toluene and β-pinene prior to ozonolysis. Ozone treatment should suppress all β-pinene fragment ions (including the relevant fraction of m/z 91) leaving a toluene mass spectrum.

Figure 2 shows the results of the ozone pretreatment experiment for a mixture of toluene and β-pinene (30 ppbv each), where A and B are the ion profiles before the ozonolysis, and parts C and D are the FIA/MIMS results after the ozonolysis step. Shortly after the injection, a rapid rise in ion signal is observed as the compounds begin to permeate through the membrane and into the mass spectrometer. When the sample stream is replaced by the nitrogen flow, a "surge" of ion signal is observed with some compounds, followed by a slower (with respect to the onset) decay of the ion signal back to the baseline. The peak ion signal height (shortly before switching off the sample stream) has been shown to be linear with the concentration of the analyte in the sample and thus can be used for quantitative analysis. The total ion signal for toluene and β-pinene are comparable when the concentrations are the same (as determined by separate injections of each compound in nitrogen), but the selected ion signals for toluene generally appear to be freer of noise than those for β-pinene, which produces a larger number of fragment ions than toluene.

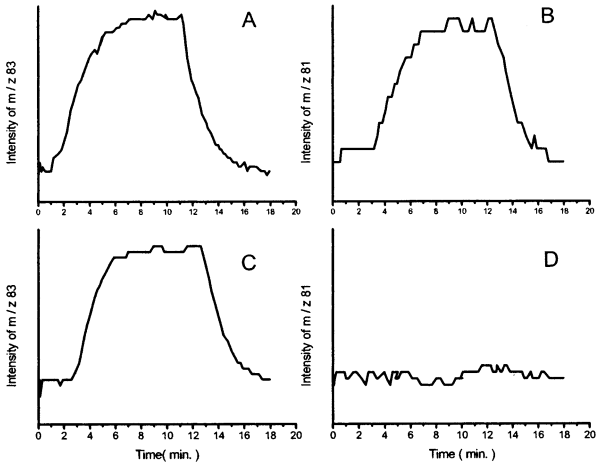

FIGURE 3. Selected ion profiles showing the signal for *m/z* 83 (cyclohexane) and *m/z* 81 (cyclohexene) from a mixture containing 1 ppmv each of cyclohexene and cyclohexane: (A) *m/z* 83 before the ozone treatment, (B) *m/z* 81 before the ozone treatment, (C) *m/z* 83 after the ozone treatment, (D) *m/z* 81 after the ozone treatment.

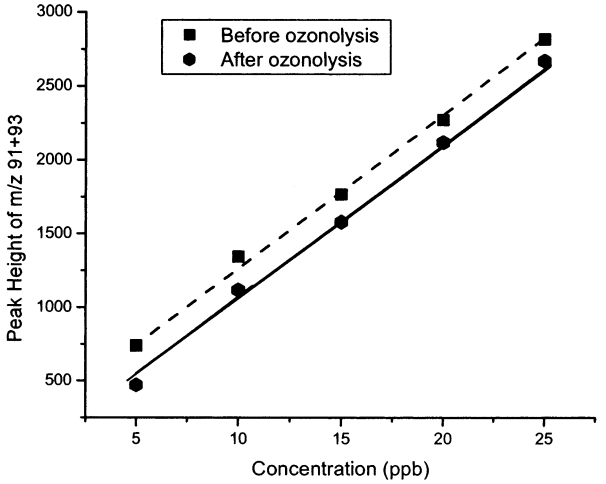

FIGURE 4. Calibration curves for toluene/β-pinene experiment: sum of peak heights for *m/z* 91 and 93 before (■) and after (◆) ozone treatment.

Comparison of Figure 2, panel D with panel B, shows clearly that β-pinene (measured as the sum of the ion signal at m/z 105, 121, and 136) is significantly suppressed because of the reaction with ozone. (Using combinations of ion signals from more than one fragment m/z for a given analyte results in superior signal to noise ratios.) Figure 2B shows the odd peak shape associated with the surge after the sampling period, when the flow of nitrogen replaces the sample flow. Since the suppression and consequent surge are not observed when oxygen is not present in the sample flow, we speculate that oxygen somehow causes a suppression of the MIMS system's response to β-pinene. We have found no reference to this effect in the literature, so we are currently investigating its origin and whether it will affect other analogous compounds. We note that β-pinene can nevertheless be measured before the onset of the signal surge (i.e., before the valve is switched to admit the nitrogen) if the calibration data is obtained in the **presence** of oxygen. Comparison of Figure 2, panel C with panel A, shows only slight suppression of the sum of the m/z 91 and 93 fragments, due to elimination of β-pinene. Ideally the m/z 91 + 93 ion signal in panel C only reflects the toluene contribution to m/z 91, allowing quantitation of the toluene. The difference between the m/z 105 + 121 + 136 selected ion profiles before and after the ozone treatment allows measurement of the β-pinene in the mixture.

Next, a mixture of cyclohexene and cyclohexane was investigated to determine whether ozone modulation was possible with hydrocarbons having similar physical properties and structures apart from the existence of a double bond. The ozone modulation experiments were conducted by examining the ion profile produced during the FIA experiments for selected fragments: m/z 81 for cyclohexene and m/z 83 for cyclohexane. These ions are essentially unique for each compound since hydrocarbons do not form protonated molecules. Figure 3 illustrates the results from the ozone modulation experiment: as before, panels A and B show the ion profiles of m/z 83 and 81 from the mixture before treatment with ozone while panels C and D are the profiles after ozonolysis. Again, it is clear that the ion signal from the unsaturated species is quantitatively blocked, while that of the alkane is essentially unaffected. Unfortunately, the sensitivity of the MIMS system for these two compounds was observed to be significantly less than for toluene and β-pinene, so the concentrations had to be raised to the atmospherically unrealistic level of 1 ppmv. We are currently investigating this discrimination effect, but for the purposes of these demonstration experiments, it is useful to note that quantitative modulation of ppbv levels of the alkene will be much easier to accomplish if the sensitivity problem can be addressed.

To demonstrate that the sensitivity problem is inherent to cyclohexene and also to test the validity of the underlying assumption of the ozone modulation—that polar carbonyl compounds are blocked by the membrane—control experiments were conducted with cyclohexene/cyclohexanone mixtures. As expected, the FIA/MIMS signals from cyclohexene in these mixtures were identical to those for equal concentration in the cyclohexene/cyclohexane mixtures. And, as predicted, no FIA/MIMS signals from cyclohexanone could be detected, even at 100 ppmv levels of the ketone.

Quantitation. Figure 4 shows calibration curves of the sum of the peak ion signals for m/z 91 and 93 from FIA/MIMS profiles for an equimolar mixture of toluene and β-pinene both before and after ozone treatment. The data demonstrate the linearity of the response ($R^2 > 0.97$) down to low ppbv for these compounds. The signal difference from ozonolysis at any given concentration is primarily due to suppression of β-pinene fragments. Thus the ion signal after ozonolysis for m/z 91 + 93 (or just for m/z 91) can be used to measure toluene, while the difference between the before and the after ozonolysis ion signals for any of the fragment ions of β-pinene can be used to quantify it.

The observed difference in ion signal for m/z 91 before and after ozonolysis is slightly larger than would be predicted by the loss of β-pinene signal (as calculated by comparison to the observed changes in the sum m/z 105 + 121 + 136 and their known ratio to m/z 91), indicating some toluene loss (<2%). Similar degradation of the cyclohexane was also observed in the cyclohexane/cyclohexene experiments. The origin of this effect was explored by kinetic modeling, presented in the next section. Despite this problem, the linearity of response in Figure 4 proves that calibration curves of unmodulated compounds may be constructed by measuring their response in the presence of ozone. Alternatively, the saturated and aromatic compounds could be measured by the method of standard addition, which is probably preferable since it can correct for other matrix effects and is fast and efficient.

Kinetic Modeling. Hydroxyl radicals (OH), which are known to be products of the ozonolysis of alkenes, react rapidly with all hydrocarbons (*21*). Consideration of this reactivity adds a path for efficiently converting alkanes and aromatics to polar forms during ozonolysis, which could account for the observed loss of their signals. In fact, it is somewhat surprising that the loss is not greater since the OH

yield of many ozonolysis reactions is near unity (*21*). To assess the role of OH in these experiments, kinetic modeling was carried out, considering all possible reactions of OH and ozone with the hydrocarbons and the major products of the ozonolysis. The modeling indicates that the reactions of OH with the aromatics and alkanes do contribute some loss but that these reactions are largely suppressed by the comparatively rapid reactions of OH with the carbonyl products of ozonolysis. The modeling results are in approximate agreement with our observed loss of "unreactive" compounds, which is all that could be expected given that many of the key rate coefficients are unknown and had to be estimated by comparison with similar reaction types.

This study demonstrates that modulation of unsaturated hydrocarbons is possible using an ozonolysis pretreatment step with MIMS. It also shows the utility of the method in analysis of mixtures with overlapping mass spectral peaks, like the toluene and β-pinene. Current work seeks to increase the sensitivity of the method using trapping and/or chemical ionization approaches. The automation of the complete system is also being improved, which would be useful if the instrument were to be used for field studies.

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